

## EMULSIFIER BLEND REPLACEMENT FOR NATURAL SODIUM SULFONATES IN METALWORKING APPLICATIONS

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### FIELD OF INVENTION

This invention relates to novel emulsifier blend of a synthetic alkyl arenesulfonate and a particular salt from a coupled reaction product of a high molecular weight polycarboxylic acylating agent, a lower molecular weight polycarboxylic acylating agent, and a coupling agent. The novel emulsifier blend is useful in other functional fluids. The functional fluids are oil-in-water emulsions, which contain water, an oil, the emulsifying composition; and functional components suitable for the application. These functional fluids may be used for many applications including, but not limited to, metalworking, metal finishing, metal quenching, heat transfer, mold release, and hydraulic applications. The utility is determined by the functional component or components added.

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### BACKGROUND OF THE INVENTION

Hydrocarbyl-substituted carboxylic acylating agents having from a few carbon atoms to at least about 30 aliphatic carbon atoms in the substituent are known. Salts of these materials are used as dispersants for lubricating oils and to make oil in water and water in oil emulsions. Reaction products of a high molecular weight acylating agent, a lower molecular weight acylating agent, and a coupler and their salts are disclosed in U.S. Patents 5,422,024 and 5,670,081 for use in functional fluids such as metalworking fluids. Claim 57 of U.S. Patent 5,670,081 further discloses that functional components selected from petroleum or synthetic alkyl sulfonates may be used with salts coupled high molecular weight acylating agents, lower molecular weight acylating agents and a coupler.

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### SUMMARY OF THE INVENTION

The present invention provides for a novel blend of a synthetic alkyl arenesulfonate and a particular salt of a reaction product of a (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating

agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of from about  
5 6 up to about 19 carbon atoms, and said components (A)(I) and (B)(I) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino  
10 group and at least one hydroxyl group. The particular salt of said reaction product is formed using components (A)(II) and (B)(II) which supply the counter ions for the salt of the high and low molecular weight polycarboxylic acylating agent. In a preferred embodiment the ratio of the equivalents of the (B)(I) to (A)(I) is in the range centered around 2.5:1 or from about 2:1 to  
15 about 3:1. This ratio of equivalents of (B)(I) to (A)(I) could be achieved in many different ways. The preferred ratio of high and low molecular weight species could be established early in the selection of the molecular weight of the starting materials or the ratio could be established later such as after partial or complete synthesis and salting of the reaction product by mixing  
20 reaction products derived from other ratios of (B)(I) to (A)(I). In a preferred composition the salt is formed with triethanolamine as the counter ion (cation) for the salt. These blends of a synthetic alkyl arenesulfonate and the particular salt are useful as emulsifiers in oil-in-water emulsions, and are particularly useful in forming functional fluid emulsions.

25 The novel blend of this invention thus functions as a replacement for natural petroleum sulfonates which has been one of the primary emulsifiers of functional fluids including metalworking fluids. The synthetic alkyl arenesulfonates by themselves do not have as much aromatic and cycloaliphatic nature as natural petroleum sulfonates nor do they have quite  
30 as broad a compositional variation of natural sulfonates. It is not fully understood why, but the synthetic alkyl arenesulfonates tend not to effectively self-emulsify oil in water (emulsify without the requirement of a

high shear mixing process). The blend of synthetic alkyl arenesulfonate and the salt of the reaction product of (A)(I), (B)(I), and C, has similar hard water stability to natural petroleum sulfonates.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 Blends of a synthetic alkyl arenesulfonate and a salt of a coupled reaction product from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarbyl substituent having an average of from about 20 to about 500 carbon atoms, (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said  
10 acylating agent (B)(I) optionally having at least one hydrocarbyl substituent having an average of from about 6 up to about 19 carbon atoms, and said components (A)(I) and (B)(I) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least  
15 one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group form useful emulsifiers for functional fluids including metalworking fluids.

The salt of the coupled reaction product will hereafter be referred to as a polyolefin ester/salt meaning that the high and low molecular weight  
20 substituents on the acylating agent are broadly polyolefins and the polyol coupling component reacts with the acylating agent to form ester linkages and the reaction of a carboxylic group of the acylating agent with a cationic species such as an alkali metal, alkaline metal, amine, aminoalcohol, or ammonium cation forms a salt. It is understood that the coupled reaction  
25 product could be a polyolefin esteramide/salt or polyolefin amide/salt if C is an aminoalcohol or polyamine.

The synthetic alkyl arenesulfonate generally comprises a broad range of reaction products from alkylating aromatic molecules such as benzene and then sulfonating that reaction product. Some people  
30 distinguish between branched alkyl benzenes and linear alkyl benzenes due to perceived differences between them. For the purposes of this application synthetic alkyl arenesulfonates can be derived from linear or branched alkyl

aromatics or from blends thereof. These synthetic alkyl arenesulfonates are available commercially from a variety of sources. A preferred subgroup of the synthetic alkyl aryl sulfonates are C<sub>6</sub> to C<sub>40</sub> alkyl benzene sulfonates, more desirably C<sub>8</sub> to C<sub>30</sub> alkyl benzene sulfonates, and preferably C<sub>10</sub> to C<sub>20</sub> alkyl benzene sulfonates and preferably linear alkyl groups. The carbon atom range specified are for the alkyl group(s) attached to the arenesulfonate. In preferred embodiments where the particular oil or oil blend used in the emulsion is known, the particular synthetic alkyl arenesulfonate will be selected based on its ability to lower the interfacial surface tension between the particular oil or oil blend and the aqueous phase to a low value, optionally to zero interfacial tension. The synthetic alkyl arenesulfonates are salts and thus include a counter ion. Typically the counter ion for the sulfonate is sodium but it may be other available counter ions or it could be partially or fully replaced by the counter ions of the salt reaction product of (A)(I), (B)(I), and C. These products are well known to the industry. The reactions to form the salt of the high molecular weight acylating agent, lower molecular weight acylating agent, and the coupler are explained later.

In preferred embodiments the higher molecular weight acylating agent is a polyisobutylene of about 500 to about 2000 number average molecular weight grafted to a succinic anhydride or succinic acid. This can be salted with a variety of counter ions. In the same preferred embodiment the lower molecular weight acylating agent is a C<sub>6</sub> to C<sub>19</sub> alkyl grafted to a succinic acid or succinic anhydride. This can be coupled with a polyamine or a polyol such as ethylene glycol (a preferred polyol). In a preferred embodiment the source of the counter ion for the salt is triethanolamine. As will be explained later, these preferred embodiments can be modified to other preferred embodiments that may exhibit equivalent or improved results.

The term "emulsion" as used in this specification and in the appended claims is intended to cover oil-in-water emulsions of sufficient fluidity to be useful as functional fluids.

The term "hydrocarbyl" is used herein to include:

(1) hydrocarbyl groups, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic groups and the like as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated groups may together form an alicyclic group);

(2) substituted hydrocarbyl groups, that is, those groups containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl nature of the hydrocarbyl group; those skilled in the art will be aware of such groups, examples of which include ether, oxo, halo (e.g., chloro and fluoro), alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.;

(3) hetero groups, that is, groups which, while having predominantly hydrocarbyl character within the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as pyridyl, furanyl, thiophenyl, imidazolyl, etc.

In general, no more than about three nonhydrocarbon groups or heteroatoms and preferably no more than one will be present for each ten carbon atoms in a hydrocarbyl group. Typically, there will be no such groups or heteroatoms in a hydrocarbyl group and it will, therefore, be purely hydrocarbyl.

The hydrocarbyl groups are preferably free from acetylenic unsaturation; ethylenic unsaturation, when present will generally be such that there is no more than one ethylenic linkage present for every ten carbon-to-carbon bonds. The hydrocarbyl groups are often completely saturated and therefore contain no ethylenic unsaturation.

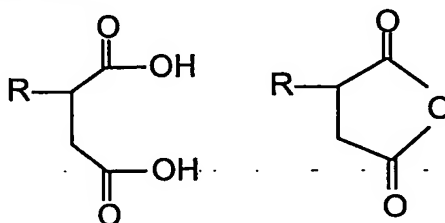
The term "lower" as used herein in conjunction with terms such as alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

Components (A)(I) and (B)(I) of Polyolefin Ester/Salt

The carboxylic acylating agents (A)(I) and (B)(I) are aliphatic or aromatic, polycarboxylic acids or acid-producing compounds. Throughout this specification and in the appended claims, the term "carboxylic acylating agent" is intended to include carboxylic acids as well as acid-producing derivatives thereof such as anhydrides, esters, acyl halides and mixtures thereof, unless otherwise specifically stated. The acylating agents (A)(I) and (B)(I) may contain polar substituents provided that the polar substituents are not present in portions sufficiently large to alter significantly the hydrocarbon character of the acylating agent. Typical suitable polar substituents include halo, such as chloro and bromo, oxo, oxy, formyl, sulfenyl, sulfinyl, thio, nitro, etc. Such polar substituents, if present, preferably do not exceed about 10% by weight of the total weight of the hydrocarbon portion of the acylating agent, exclusive of the carboxyl groups.

Examples of low molecular weight polycarboxylic acids (B)(I) include dicarboxylic acids and derivatives such as maleic acid, maleic anhydride, chloromaleic anhydride, succinic acid, succinic anhydride, glutaric acid, glutaric anhydride, adipic acid, pimelic acid, azelaic acid, sebacic acid, glutaconic acid, citraconic acid, itaconic acid, alkyl succinic acid, tetrapropylene-substituted succinic anhydride, etc. Lower alkyl esters of these acids can also be used.

Low molecular weight hydrocarbyl-substituted succinic acid and anhydrides can also be used. These succinic acids and anhydrides can be represented by the formulae:



wherein R is a C<sub>1</sub> to about a C<sub>18</sub> or C<sub>19</sub> hydrocarbyl group, more desirably a C<sub>6</sub> to C<sub>18</sub> hydrocarbyl and preferably a C<sub>10</sub> to C<sub>18</sub> hydrocarbyl. Preferably, R

is an aliphatic (branched or linear) or alicyclic hydrocarbyl group with less than about 10% of its carbon-to-carbon bonds being unsaturated. R can be derived from olefins of from 2 to about 18 or 19 carbon atoms with alpha-olefins being particularly useful. Examples of such olefins include ethylene, propylene, 1-butene, isobutene, 1-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 1-hexene, 1-heptene, 1-octene, styrene, 1-nonene 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, etc. Commercially available alpha olefin fractions such as C<sub>12-18</sub> alpha-olefins, C<sub>12-16</sub> alpha-olefins, C<sub>14-16</sub> alpha-olefins, C<sub>14-18</sub> alpha-olefins, C<sub>16-18</sub> alpha-olefins, etc., are particularly useful; these commercial alpha-olefin fractions also usually include minor amounts of alpha-olefins outside the given ranges. The production of such substituted succinic acids and their derivatives is well known to those of skill in the art and need not be discussed in detail herein.

Acid halides of the aforescribed low-molecular weight polycarboxylic acids can be used as the low-molecular weight acylating agents (B)(I) of this invention. These can be prepared by the reaction of such acids or their anhydrides with halogenating agents such as phosphorus tribromide, phosphorus pentachloride, phosphorus oxychloride or thionyl chloride. Esters of such acids can be prepared simply by the reaction of the acid, acid halide or anhydride with an alcohol or phenolic compound. Particularly useful are the lower alkyl and alkenyl alcohols such as methanol, ethanol, allyl alcohol, propanol, cyclohexanol, etc. Esterification reactions are usually promoted by the use of alkaline catalysts such as sodium hydroxide or alkoxide, or an acidic catalyst such as sulfuric acid or toluene sulfonic acid.

Although it is preferred that the acylating agent (B)(I) is an aliphatic polycarboxylic acid, and more preferably a dicarboxylic acid, the carboxylic acylating agent (B)(I) may also be an aromatic polycarboxylic acid or acid-producing compound. The aromatic acids are preferably dicarboxy-substituted benzene, naphthalene, anthracene, phenanthrene or like aromatic hydrocarbons. They include also the alkyl-substituted derivatives,

and the alkyl groups may contain up to about 12 carbon atoms. The aromatic acid may also contain other substituents such as halo, hydroxy, lower alkoxy, etc. Specific examples of aromatic polycarboxylic acids and acid-producing compounds useful as acylating agent (B)(I) include phthalic acid, isophthalic acid, terephthalic acid, 4-methyl-benzene-1,3-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, anthracene dicarboxylic acid, 3-dodecyl-benzene-1,4-dicarboxylic acid, 2,5-dibutylbenzene-1,4-dicarboxylic acid, etc. The anhydrides of these dicarboxylic acids also are useful as the carboxylic acylating agent (B)(I).

The high-molecular weight polycarboxylic acylating agents (A)(I) are well known in the art and have been described in detail, for example, in the following U.S., British and Canadian patents: U.S. Pat. Nos. 3,024,237; 3,087,936; 3,163,603; 3,172,892; 3,215,707; 3,219,666; 3,231,587; 3,245,910; 3,254,025; 3,271,310; 3,272,743; 3,272,746; 3,278,550; 3,288,714; 3,306,907; 3,307,928; 3,312,619; 3,341,542; 3,346,354; 3,367,943; 3,373,111; 3,374,174; 3,381,022; 3,394,179; 3,454,607; 3,346,354; 3,470,098; 3,630,902; 3,652,616; 3,755,169; 3,868,330; 3,912,764; 4,234,435; and 4,368,133; British Patents 944,136; 1,085,903; 1,162,436; and 1,440,219; and Canadian Patent 956,397. These patents are incorporated herein by reference.

As disclosed in the foregoing patents, there are several processes for preparing these high-molecular weight acylating agents (A)(I). Generally, these processes involve the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, anhydride or ester reactant with (2) an ethylenically unsaturated hydrocarbon containing at least about 20 aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about 20 aliphatic carbon atoms at a temperature within the range of about 100° to about 300°C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant preferably contains at least about 30 carbon atoms, more preferably at least about 40 carbon atoms, more preferably at least about 50 carbon atoms, and may contain polar substituents, oil-solubilizing



pendant groups, and be unsaturated within the general limitations explained hereinabove.

When preparing the carboxylic acid acylating agent, the carboxylic acid reactant usually corresponds to the formula  $R_o - (COOH)_n$ , where  $R_o$  is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and  $n$  is an integer from 2 to about 6 and preferably is 2. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, ester, or other equivalent acylating agent and mixtures of two or more of these. Ordinarily, the total number of carbon atoms in the acidic reactant will not exceed about 20, preferably this number will not exceed about 10 and generally will not exceed about 6, exclusive of the carboxyl-based groups. Preferably the acidic reactant will have at least one ethylenic linkage in an alpha, beta-position with respect to at least one carboxyl function. Exemplary acidic reactants are maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, chloromaleic acid, aconitic acid, and the like. Preferred acid reactants include maleic acid and maleic anhydride.

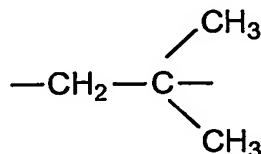
The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of these high-molecular weight carboxylic acylating agents (A)(I) are preferably high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. Polymers and chlorinated polymers derived from mono-olefins having from 2 to about 30 carbon atoms are preferred. Especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene. Polymers from isobutylene are preferred.

Interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic

olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsaturated reactant. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with  
 5 piperylene, isobutene with chloroprene, isobutene with p-methyl-styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl- 1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, etc.

For reasons of hydrocarbon solubility, the interpolymers contemplated  
 10 for use in preparing the acylating agents of this invention are preferably substantially aliphatic and substantially saturated, that is, they should contain at least about 80% and preferably about 95%, on a weight basis, of units derived from aliphatic mono-olefins. Preferably, they will contain no more than about 5% olefinic linkages based on the total number of the carbon-to-  
 15 carbon covalent linkages present.

In one embodiment of the invention, the polymers and chlorinated polymers are obtained by the polymerization of a C<sub>4</sub> refinery stream having a butene content of about 35% to about 75% by weight and an isobutene content of about 30% to about 60% by weight in the presence of a Lewis  
 20 acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutenes preferably contain predominantly (that is, greater than about 80% of the total repeat units) isobutene repeat units of the configuration.



25 The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the higher molecular weight carboxylic acylating agents preferably have up to about 500 carbon atoms per molecule. Preferred acylating agents (A)(I) are those containing hydrocarbyl groups of from about 20 to about 500 carbon atoms, more  
 30 preferably from about 30 to about 500 carbon atoms, more preferably from

about 40 to about 500 carbon atoms, more preferably from about 50 to about 500 carbon atoms.

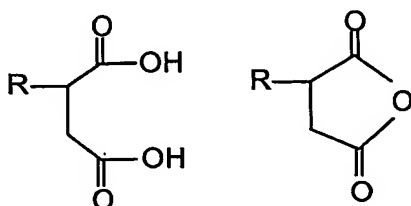
The polycarboxylic acid acylating agents (A)(I) can also be obtained by reacting chlorinated polycarboxylic acids, anhydrides, acyl halides, and  
5 the like with ethylenically unsaturated hydrocarbons or ethylenically unsaturated substituted hydrocarbons such as the polyolefins and substituted polyolefins described hereinbefore in the manner described in U.S. Pat. No. 3,340,281, this patent being incorporated herein by reference.

The high-molecular weight polycarboxylic acid anhydrides (A)(I) can  
10 be obtained by dehydrating the corresponding acids. Dehydration is readily accomplished by heating the acid to a temperature above about 70°C, preferably in the presence of a dehydration agent, e.g., acetic anhydride. Cyclic anhydrides are usually obtained from polycarboxylic acids having acid groups separated by no more than three carbon atoms such as substituted  
15 succinic or glutaric acid, whereas linear anhydrides are usually obtained from polycarboxylic acids having the acid groups separated by four or more carbon atoms.

The acid halides of the polycarboxylic acids can be prepared by the reaction of the acids or their anhydrides with a halogenating agent such as  
20 phosphorus tribromide, phosphorus pentachloride, or thionyl chloride.

Hydrocarbyl-substituted succinic acids and the anhydride, acid halide and ester derivatives thereof are particularly preferred acylating agents (A)(I). These acylating agents are preferably prepared by reacting maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon  
25 such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature in the range of about 100°C to about 300°C, preferably, about 100°C to about 200°C. The product from this reaction is a hydrocarbyl-substituted succinic anhydride wherein the substituent is derived from the olefin or chlorinated hydrocarbon. The product may be  
30 hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages by standard hydrogenation procedures, if desired. The hydrocarbyl-substituted succinic anhydrides may be hydrolyzed by treatment

with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid halide or ester by reacting with a phosphorus halide, phenol or alcohol. The hydrocarbonyl-substituted succinic acids and anhydrides (A)(I) can be represented by the formulae:



wherein R is the hydrocarbonyl substituent. Preferably R contains from about 20 to about 500 carbon atoms, more preferably from about 30 to about 500 carbon atoms, more preferably from about 40 to about 500 carbon atoms, more preferably from about 50 to about 500 carbon atoms.

Although it is preferred that the acylating agent (A)(I) is an aliphatic polycarboxylic acid, and more preferably a dicarboxylic acid, the carboxylic acylating agent (A)(I) may also be an aromatic polycarboxylic acid or acid-producing compound. The aromatic acids are preferably alkyl-substituted, dicarboxy-substituted benzene, naphthalene, anthracene, phenanthrene or like aromatic hydrocarbons. The alkyl groups may contain up to about 30 carbon atoms. The aromatic acid may also contain other substituents such as halo, hydroxy, lower alkoxy, etc.

#### 20      Component (C) of Polyolefin Ester/Salt:

The (C) component acts as a bridge between the low (B)(I) and the high (A)(I) molecular weight succinic acid molecules. The low and high molecular weight molecules may be mixed together, and are reacted with the bridging molecule. The reaction is such that the preferred species in the reaction mixture is the product in which a (C) molecule acts as a bridge between a lower molecular weight (B) species and a high molecular weight (A) species or between two lower molecular weight (B) species. However, there is formation of molecules in which two low molecular weight succinic agents are linked as well as formation of species in which two high molecular

weight succinic agents are linked. In this case, the ratio between the ratio of equivalents between (B)(I) and (A)(I) is 2.5:1 or larger. If the statistical distribution of products is formed, at a ratio of (B)(I) to (A)(I) of 2: 1, the number of molecules in which (A)(I) is linked to (B)(I) equals the number of molecules where (B)(I) is linked to (B)(I). At a ratio of (B)(I) to (A)(I) of 2.5:1 or larger, (B)(I) linked to (B)(I) becomes the predominant species. In preferred embodiments the ratio of (B)(I) to (A)(I) is from about 1:1 to about 4:1 and more preferably from about 2:1 to about 3:1.

Component (C) can be any compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups, or (v) at least one primary or secondary amino group and at least one hydroxyl group. These include polyamines, polyols and hydroxyamines. In a preferred embodiment component C has two hydroxyl groups. In a more preferred embodiment component C is ethylene glycol.

(1) Polyamines Useful as Component (C) of Polyolefin Ester/Salt

The polyamines useful as component (C) are characterized by the presence within their structure of at least two  $\text{-NH}_2$  groups, at least two  $\text{>NH}$  groups, or at least one  $\text{-NH}_2$  group and at least one  $\text{>NH}$  group.

These polyamines can be aliphatic, cycloaliphatic, aromatic or heterocyclic, including aliphatic-substituted aromatic, aliphatic-substituted cycloaliphatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and heterocyclic-substituted aromatic amines. These amines may be saturated or unsaturated. If unsaturated, the amine is preferably free from acetylenic unsaturation. These amines may also contain non-hydrocarbon substituents or groups as long as these groups do not significantly interfere with the reaction of such amines with reactants (A)(I) and (B)(I). Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting

groups such as  $-O-$  and  $-S-$  (e.g., as in such groups as  $-CH_2CH_2-X-CH_2CH_2-$  where X is  $-O-$  or  $-S-$ ).

The polyamines include aliphatic, cycloaliphatic and aromatic polyamines analogous to the aliphatic, cycloaliphatic and aromatic  
5 monoamines described below except for the presence within their structure of at least one additional  $>NH$  or  $-NH_2$  group.

Aliphatic monoamines include mono-aliphatic and di-aliphatic-substituted amines wherein the aliphatic groups can be saturated or unsaturated and straight or branched chain. Thus, they are primary or  
10 secondary aliphatic amines. Such amines include, for example, mono- and di-alkyl-substituted amines, mono- and di-alkenyl-substituted amines, and amines having one N-alkenyl substituent and one N-alkyl substituent, and the like. The total number of carbon atoms in these aliphatic monoamines preferably does not exceed about 40 and usually does not exceed about 20  
15 carbon atoms. Specific examples of such monoamines include ethylamine, di-ethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl-laurylamine, oleylamine, N-methyl-octylamine, dodecylamine, octadecylamine, and the like. Examples of cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic  
20 amines, and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine, benzylamine, phenylethylamine, and 3-(furylpropyl) amine.

Cycloaliphatic monoamines are those monoamines wherein there is one cycloaliphatic substituent attached directly to the amino nitrogen through  
25 a carbon atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines, N-ethyl-cyclohexylamines, dicyclohexylamines, and the like. Examples of aliphatic-substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic  
30 monoamines include propyl-substituted cyclohexyl-amines, phenyl-substituted cyclopentylamines and pyran-yl-substituted cyclohexylamine.

Aromatic monoamines include those monoamines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those  
5 derived from naphthalene. Examples of aromatic monoamines include aniline, di(para-methylphenyl) amine, naphthylamine, N-(n-butyl) aniline, and the like. Examples of aliphatic-substituted, cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines include para-ethoxyaniline, paradodecylamine, cyclohexyl-substituted naphthylamine and thienyl-  
10 substituted aniline.

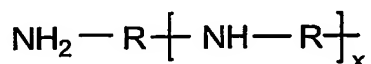
Heterocyclic polyamines can also be used. As used herein, the terminology "heterocyclic polyamine" is intended to describe those heterocyclic amines containing at least two primary amino groups, at least two secondary amino groups, or at least one of each, and at least one  
15 nitrogen as a heteroatom in the heterocyclic ring. As long as there is present in the heterocyclic polyamines at least two primary amino groups, at least two secondary amino groups, or at least one of each, the hetero-N atom in the ring can be a tertiary amino nitrogen; that is, one that does not have hydrogen attached directly to the ring nitrogen. The hetero-N atom can be  
20 one of the secondary amino groups; that is, it can be a ring nitrogen with hydrogen directly attached to it. Heterocyclic amines can be saturated or unsaturated and can contain various substituents such as nitro, alkoxy, alkyl mercapto, alkyl, alkenyl, aryl, alkaryl, or aralkyl substituents. Generally, the total number of carbon atoms in the substituents will not exceed about 20.  
25 Heterocyclic amines can contain heteroatoms other than nitrogen, especially oxygen and sulfur. Obviously they can contain more than one nitrogen heteroatom. The 5- and 6-membered heterocyclic rings are preferred.

Among the suitable heterocyclic polyamines are the aziridines, azetidines, azolidines, tetra- and di-hydro pyridines, pyrroles, indoles,  
30 piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-diaminoalkyl-

piperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro-derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Useful heterocyclic polyamines are the saturated 5- and 6-membered heterocyclic polyamines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminoethylpiperazine and N,N'-diaminoethylpiperazine.

Hydrazine and substituted-hydrazines can also be used. The substituents which may be present on the hydrazine include alkyl, alkenyl, aryl, aralkyl, alkaryl, and the like. Usually, the substituents are alkyl, especially lower alkyl, phenyl, and substituted phenyl such as lower alkoxy-substituted phenyl or lower alkyl-substituted phenyl. Specific examples of substituted hydrazines are methylhydrazine, N,N-dimethylhydrazine, N,N'-dimethylhydrazine, phenylhydrazine, N-phenyl- N'-ethylhydrazine, N-(para-tolyl)-N'-(n-butyl)-hydrazine, N-(paranitrophenyl)-hydrazine, N-(para-nitrophenyl)-N-methylhydrazine, N,N'-di-(para-chlorophenyl)-hydrazine, N-phenyl-N'-cyclohexylhydrazine, and the like.

Another group of amines suitable for use in this invention are branched polyalkylene polyamines. The branched polyalkylene polyamines are polyalkylene polyamines wherein the branched group is a side chain containing on the average at least one nitrogen-bonded aminoalkylene

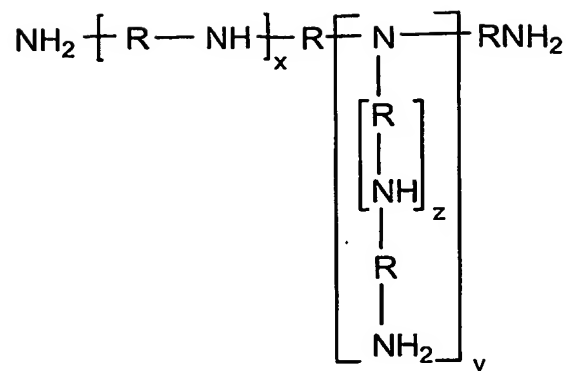


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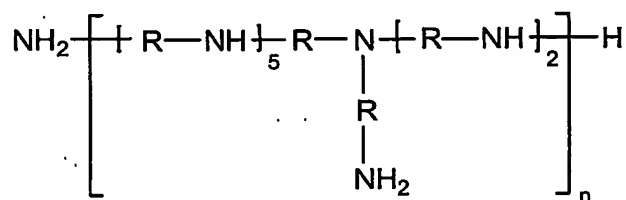
group per nine amino units present on the main chain; for example, 1-4 of such branched chains per nine units on the main chain, but preferably one side chain unit per nine main chain units. Thus, these polyamines contain at least three primary amino groups and at least one tertiary amino group.

30 These amines may be expressed by the formula:

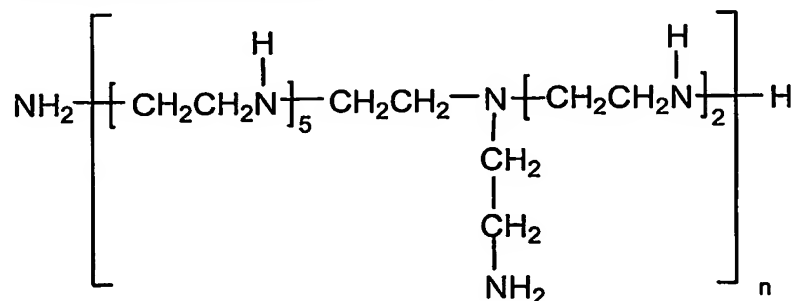




wherein R is an alkylene group such as ethylene, propylene, butylene and other homologs (both straight chained and branched), etc., but preferably ethylene; and x, y and z are integers; x is in the range of from about 4 to about 24 or more, preferably from about 6 to about 18; y is in the range of from 1 to about 6 or more, preferably from 1 to about 3; and z is in the range of from zero to about 6, preferably from zero to about 1. The x and y units may be sequential, alternative, orderly or randomly distributed. A useful class of such polyamines includes those of the formula:



wherein n is an integer in the range of from 1 to about 20 or more, preferably in the range of from 1 to about 3, and R is preferably ethylene, but may be propylene, butylene, etc. (straight chained or branched). Useful embodiments are represented by the formula:



wherein n is an integer in the range of 1 to about 3. The groups within the brackets may be joined in a head-to-head or a head-to-tail fashion. U.S. Pat. Nos. 3,200,106 and 3,259,578 are incorporated herein by reference for their disclosures relative to said polyamines.

5            Suitable polyamines also include polyoxyalkylene polyamines, e.g., polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, preferably from about 400 to 2000. Examples of these polyoxyalkylene polyamines include those amines represented by the formula:

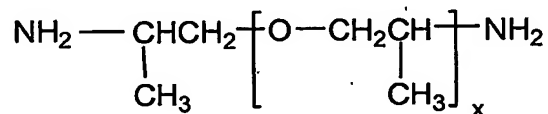
10  $\text{NH}_2$  -Alkylene- $(-\text{O}-\text{Alkylene}-)_m \text{NH}_2$

wherein m has a value of from about 3 to about 70, preferably from about 10 to about 35.

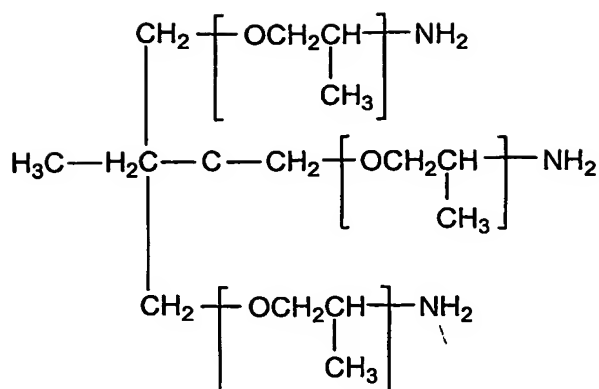
$$\text{R-[Alkylene-(-O-Alkylene-)}_n \text{NH}_2 \text{ ]}_{3-6}$$

wherein n is a number in the range from 1 to about 40, with the proviso that the sum of all of the n's is from about 3 to about 70 and generally from about 6 to about 35, and R is a polyvalent saturated hydrocarbyl group of up to about 10 carbon atoms having a valence of from about 3 to about 6. The alkylene groups may be straight or branched chains and contain from 1 to about 7 carbon atoms, and usually from 1 to about 4 carbon atoms. The various alkylene groups present within the above formulae may be the same or different.

More specific examples of these polyamines include:



25 wherein x has a value of from about 3 to about 70, preferably from about 10 to 35;



and wherein x+y+z have a total value ranging from about 3 to about 30, preferably from about 5 to about 10.

5            Useful polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to about 2000. The polyoxyalkylene polyamines are commercially available from the Huntsman Chemical under the trade name "Jeffamine". U.S. Pat. Nos. 3,804,763 and  
 10            3,948,800 are incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines.

Useful polyamines are the alkylene polyamines, including the polyalkylene polyamines, as described in more detail hereafter. The alkylene polyamines include those conforming to the formula:



15            wherein n is from 1 to about 10, preferably from 1 to about 7; each R and R' is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to about 700 carbon atoms,  
 20            preferably up to about 100 carbon atoms, more preferably up to about 50 carbon atoms, more preferably up to about 30 carbon atoms, with the proviso that at least one of R and at least one of R' are hydrogen; and the "Alkylene" group has from about 1 to about 18 carbon atoms, preferably from 1 to about 4 carbon atoms, with the preferred Alkylene being ethylene or

propylene. Useful alkylene polyamines are those wherein each R and each R' is hydrogen with the ethylene polyamines, and mixtures of ethylene polyamines being particularly preferred. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included.

Alkylene polyamines that are useful include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, di(trimethylene) triamine, N-(2-aminoethyl) piperazine, 1,4-bis(2-aminoethyl) piperazine, and the like. Higher homologs as are obtained by condensing two or more of the above-illustrated alkylene amines are useful as amines in this invention as are mixtures of two or more of any of the aforescribed polyamines.

Ethylene polyamines, such as those mentioned above, are described in detail under the heading "Diamines and Higher Amines, Aliphatic" in The Encyclopedia of Chemical Technology, Third Edition, Kirk-Othmer, Volume 7, pp. 580-602, a Wiley-Interscience Publication, John Wiley and Sons, 1979, these pages being incorporated herein by reference. Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia, etc. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines.

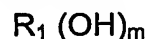
Alkoxyated alkylene polyamines (e.g., N,N'-(diethanol)-ethylene diamine) can be used. Such polyamines can be made by reacting alkylene amines (e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by reacting the afore-described primary, secondary or tertiary

alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

Specific examples of alkoxyated alkylene polyamines include N-(2-hydroxyethyl) ethylenediamine, N,N-bis(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine, di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid polyamines are also useful.

#### 15       (2) Polyols Useful as Component (C) of Polyolefin Ester/Salt

The polyols or polyhydric alcohols useful as component (C) include those compounds of the general formula:



wherein R<sub>1</sub> is a monovalent or polyvalent organic group joined to the –OH groups through carbon-to-oxygen bonds (that is, –COH wherein the carbon is not part of a carbonyl group) and m is an integer of from 2 to about 10, preferably 2 to about 6. These alcohols can be aliphatic, cycloaliphatic, aromatic, and heterocyclic, including aliphatic-substituted cycloaliphatic alcohols, aliphatic-substituted aromatic alcohols, aliphatic-substituted heterocyclic alcohols, cycloaliphatic-substituted aliphatic alcohols, cycloaliphatic-substituted heterocyclic alcohols, heterocyclic-substituted aliphatic alcohols, heterocyclic-substituted cycloaliphatic alcohols, and heterocyclic-substituted aromatic alcohols. Except for the polyoxyalkylene alcohols, the polyhydric alcohols corresponding to the formula R<sub>1</sub> (OH)<sub>m</sub> preferably contain not more than about 40 carbon atoms, more preferably not more than about 20 carbon atoms. The alcohols may contain non-hydrocarbon substituents or groups which do not interfere with the reaction

of the alcohols with the hydrocarbyl-substituted carboxylic acids or anhydrides of this invention. Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting groups such as  $-O-$  and  $-S-$  (e.g., as in such groups as  $-CH_2 CH_2 -XCH_2 CH_2$  where X is  $-O-$  or  $-S-$ ).

Useful polyoxyalkylene alcohols and derivatives thereof include the hydrocarbyl ethers and the carboxylic acid esters obtained by reacting the alcohols with various carboxylic acids. Illustrative hydrocarbyl groups are alkyl, cycloalkyl, alkylaryl, aralkyl, alkylaryl alkyl, etc., containing up to about 40 carbon atoms. Specific hydrocarbyl groups include methyl, butyl, dodecyl, tolyl, phenyl, naphthyl, dodecylphenyl, p-octylphenyl ethyl, cyclohexyl, and the like. Carboxylic acids useful in preparing the ester derivatives are mono- or polycarboxylic acids such as acetic acid, valeric acid, lauric acid, stearic acid, succinic acid, and alkyl or alkenyl-substituted succinic acids wherein the alkyl or alkenyl group contains up to about 20 carbon atoms. Members of this class of alcohols are commercially available from various sources; e.g., PLURONICS, polyols available from Wyandotte Chemicals Corporation; POLYGLYCOL 112-2, a liquid triol derived from ethylene-oxide and propylene-oxide available from Dow Chemical Co.; and TERGITOLS, dodecylphenyl or nonylphenyl polyethylene glycol ethers, and UCONS, polyalkylene glycols and various derivatives thereof, both available from Union Carbide Corporation. However, the alcohols used must have an average of at least one free alcoholic hydroxyl group per molecule of polyoxyalkylene alcohol. For purposes of describing these polyoxyalkylene alcohols, an alcoholic hydroxyl group is one attached to a carbon atom that does not form part of an aromatic nucleus.

Alcohols useful in this invention also include alkylene glycols and polyoxyalkylene alcohols such as polyoxyethylene alcohols, polyoxypropylene alcohols, polyoxybutylene alcohols, and the like. These polyoxyalkylene alcohols (sometimes called polyglycols) can contain up to about 150 oxyalkylene groups, with the alkylene group containing from about 2 to about 8 carbon atoms. Such polyoxyalkylene alcohols are generally

dihydric alcohols. That is, each end of the molecule terminates with an OH group. In order for such polyoxyalkylene alcohols to be useful, there must be at least two OH groups.

The polyhydric alcohols useful in this invention include polyhydroxy aromatic compounds. Polyhydric phenols and naphthols are useful hydroxyaromatic compounds. These hydroxy-substituted aromatic compounds may contain other substituents in addition to the hydroxy substituents such as halo, alkyl, alkenyl, alkoxy, alkylmercapto, nitro and the like. Usually, the hydroxy aromatic compound will contain from 2 to about 4 hydroxy groups. The aromatic hydroxy compounds are illustrated by the following specific examples: resorcinol, catechol, p,p'-dihydroxy-biphenyl, hydroquinone, pyrogallol, phloroglucinol, hexylresorcinol, orcinol, etc.

The polyhydric alcohols preferably contain from 2 to about 4 or 10 hydroxy groups. They are illustrated, for example, by the alkylene glycols and polyoxyalkylene glycols mentioned above such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyoxyalkylene glycols in which the alkylene groups contain from 2 to about 8 carbon atoms.

Other useful polyhydric alcohols include glycerol, monooleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, n-butyl ester of 9, 10-dihydroxy stearic acid, methyl ester of 9, 10-dihydroxy stearic acid, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, and xylene glycol. Carbohydrates such as sugars, starches, celluloses, and so forth likewise can be used. The carbohydrates may be exemplified by glucose, fructose, sucrose, rhamnose, mannose, glyceraldehyde, and galactose.

Polyhydric alcohols having at least 3 hydroxyl groups, some, but not all of which have been esterified with an aliphatic monocarboxylic acid having from about 8 to about 30 carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid or tall oil acid are useful.

Further specific examples of such partially esterified polyhydric alcohols are the monooleate of sorbitol, distearate of sorbitol, monooleate of glycerol, monostearate of glycerol, di-dodecanoate of erythritol, and the like.

Useful alcohols also include those polyhydric alcohols containing up to about 12 carbon atoms, and especially those containing from about 3 to about 10 carbon atoms. This class of alcohols includes glycerol, erythritol, pentaerythritol, dipentaerythritol, gluconic acid, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, quinic acid, 2,2,6,6-tetrakis-(hydroxymethyl)cyclohexanol, 1,10-decanediol, digitalose, and the like. Aliphatic alcohols containing at least about 3 hydroxyl groups and up to about 10 carbon atoms are useful.

Useful polyhydric alcohols are the polyhydric alkanols containing from about 3 to about 10 carbon atoms and particularly, those containing about 3 to about 6 carbon atoms and having at least three hydroxyl groups. Such alcohols are exemplified by glycerol, erythritol, pentaerythritol, mannitol, sorbitol, 2-hydroxymethyl-2-methyl-1,3-propanediol-(trimethylolethane), 2-hydroxymethyl-2-ethyl-1,3-propanediol(trimethylopropane), 1,2,4-hexanetriol, and the like.

## 20      (2) Hydroxyamines Useful as Component (C) of Polyolefin Ester/Salt

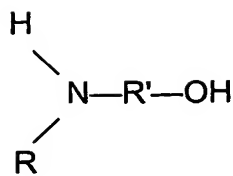
The hydroxyamines can be primary or secondary amines. They can also be tertiary amines provided said tertiary amines also contain at least two hydroxyl groups. These hydroxyamines contain at least two >NH groups, at least two -NH<sub>2</sub> groups, at least one -OH group and at least one >NH or -NH<sub>2</sub> group, or at least two -OH groups. The terms "hydroxyamine" and "aminoalcohol" describe the same class of compounds and, therefore, can be used interchangeably.

The hydroxyamines can be primary or secondary alkanol amines or mixtures thereof. Such amines can be represented, respectively, by the formulae:





and

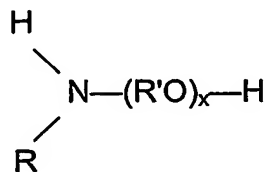


wherein R is a hydrocarbyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbyl group of two to about eight carbon atoms and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms. The group -R'-OH in such formulae represents the hydroxyl-substituted hydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Typically, R is a lower alkyl group of up to seven carbon atoms.

The hydroxyamines can also be ether containing N-(hydroxy-substituted hydrocarbyl)amines. These are hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described primary and secondary alkanol amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines can be conveniently prepared by reaction of epoxides with afore-described amines and can be represented by the formulae:



and



wherein x is a number from about 2 to about 15 and R and R' are as described above.

Polyamine analogs of these hydroxy amines, particularly alkoxyated alkylene polyamines (e.g., N,N-(diethanol)-ethylene diamine) can also be

used. Such polyamines can be made by reacting alkylene amines (e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by  
5 reacting the afore-described primary or secondary alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

Specific examples of alkoxyated alkylene polyamines include N-(2-  
10 hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine, di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy alkylene polyamines through  
15 amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid mono- or polyamines are also useful.

Examples of the N-(hydroxyl-substituted hydrocarbyl) amines include  
20 mono-, di-, and triethanol amine (highly preferred in some embodiments), diethylethanol amine, di-(3-hydroxyl propyl) amine, N-(3-hydroxyl butyl) amine, N-(4-hydroxyl butyl) amine, N,N-di-(2-hydroxyl propyl) amine, N-(2-hydroxyl ethyl) morpholine and its thio analog, N-(2-hydroxyl ethyl)  
25 cyclohexyl amine, N-3-hydroxyl cyclopentyl amine, o-, m- and p-aminophenol, N-(hydroxyl ethyl) piperazine, N,N'-di(hydroxyl ethyl) piperazine, and the like.

Further hydroxyamines are the hydroxy-substituted primary amines described in U.S. Pat. No. 3,576,743 by the general formula

30 
$$R_a - NH_2$$

wherein  $R_a$  is a monovalent organic group containing at least one alcoholic hydroxy group. The total number of carbon atoms in  $R_a$  preferably does not

exceed about 20. Hydroxy-substituted aliphatic primary amines containing a total of up to about 10 carbon atoms are useful. The polyhydroxy-substituted alkanol primary amines wherein there is only one amino group present (i.e., a primary amino group) having one alkyl substituent containing up to about 10 carbon atoms and up to about 6 hydroxyl groups are useful. These alkanol primary amines correspond to  $R_a-NH_2$  wherein  $R_a$  is a mono- or polyhydroxy-substituted alkyl group. Specific examples of the hydroxy-substituted primary amines include 2-amino-1-butanol, 2-amino-2-methyl 1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(beta-hydroxypropyl)-N'-(beta-aminoethyl)-piperazine, tris-(hydroxymethyl) amino methane (also known as trismethylolamino methane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethyl amine, glucamine, glusoamine, 4-amino-3-hydroxy-3-methyl-1-butene (which can be prepared according to procedures known in the art by reacting isoprene-oxide with ammonia), N-3-(aminopropyl)-4-(2-hydroxyethyl)piperidine, 2-amino-6-methyl-6-heptanol, 5-amino-1-pentanol, N-(beta-hydroxyethyl)1,3-diamino propane, 1,3-diamino-2-hydroxypropane, N-(beta-hydroxy ethoxyethyl) ethylenediamine, trismethylolaminomethane and the like. U.S. Pat. No. 3,576,743 is incorporated herein by reference.

Hydroxyalkyl alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful. Useful hydroxyalkyl-substituted alkylene polyamines include those in which the hydroxyalkyl group is a lower hydroxyalkyl group, i.e., having less than eight carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl)-piperazine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyl-substituted tetraethylene pentamine, N-(3-hydroxybutyl) tetramethylene diamine, etc. Higher homologs as are obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied

by removal of ammonia and condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water.

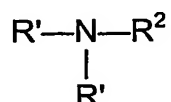
5     Components (A)(II) and (B)(II) of Polyolefin Ester/Salt (Source of Counter Ions)

Components (A)(II) and (B)(II) can be the same or different, but preferably are the same. The amines useful as component (A)(II) and (B)(II) in preparing the salt compositions of the invention include ammonia, and the primary amines, secondary amines and hydroxyamines discussed above as  
10     being useful as component (C). In addition to ammonia, the primary amines, secondary amines and hydroxyamines discussed above, the amines useful as components (A)(II) and (B)(II) also include primary and secondary monoamines, and tertiary mono- and polyamines. The primary and secondary monoamines that are useful as components (A)(II) and (B)(II) are  
15     described above under the sub-title "(1) Polyamines Useful as Component (C)" as being analogues of the polyamines described above. These primary and secondary monoamines include the aliphatic, cycloaliphatic and aromatic monoamines discussed above. The tertiary amines are analogous to the primary amines, secondary amines and hydroxyamines discussed  
20     above with the exception that they can be either monoamines or polyamines and the hydrogen atoms in the H-N< or -NH<sub>2</sub> groups are replaced by hydrocarbyl groups.

The tertiary amines can be aliphatic, cyclo-aliphatic, aromatic or heterocyclic, including aliphatic-substituted aromatic, aliphatic-substituted  
25     cycloaliphatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and heterocyclic-substituted  
30     aromatic amines. These tertiary amines may be saturated or unsaturated. If unsaturated, the amine is preferably free from acetylenic unsaturation. The tertiary amines may also contain non-hydrocarbon substituents or groups as

long as these groups do not significantly interfere with the reaction of component (B) with component (A). Such non-hydrocarbon substituents or groups include lower alkoxy, lower alkyl, mercapto, nitro, and interrupting groups such as  $-O-$  and  $-S-$  (e.g., as in such groups as  $-CH_2CH_2-X-$   
 5  $CH_2CH_2-$  where X is  $-O-$  or  $-S-$ ).

The monoamines can be represented by the formula:



10 wherein  $R'$ ,  $R$  and  $R$  are the same or different hydrocarbyl groups. Preferably,  $R'$ ,  $R$  and  $R$  are independently hydrocarbyl groups of from 1 to about 20 carbon atoms.

Examples of useful tertiary amines include trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, monomethyldiethyl amine,  
 15 monoethyldimethyl amine, dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl amine, dimethylheptyl amine, dimethyloctyl amine, dimethylnonyl amine, dimethyldecyl amine, dimethylphenyl amine, N,N-dioctyl-1-octanamine, N,N-didodecyl-1-dodecanamine tricoco amine, trihydrogenated-tallow amine, N-methyl-  
 20 dihydrogenated tallow amine, N,N-dimethyl-1-dodecanamine, N,N-dimethyl-1-tetradecanamine, N,N-dimethyl-1-hexadecanamine, N,N-dimethyl-1-octadecanamine, N,N-dimethylcocoamine, N,N-dimethylsoyaamine, N,N-dimethylhydrogenated tallow amine, etc.

Useful tertiary alkanol amines are represented by the formula:



30 wherein each R is independently a hydrocarbyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbyl group of two to about eight carbon atoms and  $R'$  is a divalent hydrocarbyl group of about two to about 18 carbon atoms. The group  $-R'-OH$  in such formula represents the

hydroxyl-substituted hydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Where two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R is a lower alkyl group of up to seven carbon atoms. The hydroxyamines can also be an ether containing N- (hydroxy-substituted hydrocarbyl)amine. These are hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines can be conveniently prepared by reaction of epoxides with afore-described amines and can be represented by the formula:



wherein x is a number from about 2 to about 15 and R and R' are as described above.

Useful polyamines include the alkylene polyamines discussed above as well as alkylene polyamines with only one or no hydrogens attached to the nitrogen atoms. Thus, the alkylene polyamines useful as components (A)(II) and (B)(II) include those conforming to the formula:



wherein n is from 1 to about 10, preferably from 1 to about 7; each R is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-

substituted hydrocarbyl group having up to about 700 carbon atoms, preferably up to about 100 carbon atoms, more preferably up to about 50 carbon atoms, more preferably up to about 30 carbon atoms; and the "Alkylene" group has from about 1 to about 18 carbon atoms, preferably from 1 to about 4 carbon atoms, with the preferred Alkylene being ethylene or propylene.

The alkali and alkaline earth metals that are useful as components (A)(II) and (B)(II) can be any alkali or alkaline earth metal. The alkali metals are preferred. Sodium and potassium are particularly preferred. The alkali and alkaline earth metal compounds that are useful include, for example, the oxides, hydroxides and carbonates. Sodium hydroxide and potassium hydroxide are particularly preferred.

#### Formation of the Salt Compositions:

The salt compositions of the invention can be prepared by initially reacting the acylating agents (A)(I) and (B)(I) with component (C) to form an intermediate, and thereafter reacting said intermediate with components (A)(II) and (B)(II) to form the desired salt. An alternative method of preparing these salt compositions involves reacting components (A)(I) and (A)(II) with each other to form a first salt moiety, separately reacting components (B)(I) and (B)(II) with each other to form a second salt moiety, then reacting a mixture of these two salt moieties with component (C).

The ratio of reactants utilized in the preparation of the inventive salt compositions may be varied over a wide range. Generally, for each equivalent of each of the acylating agents (A)(I) and (B)(I), at least about one equivalent of component (C) is used. From about 0.1 to about 2 equivalents or more of components (A)(II) and (B)(II) are used for each equivalent of components (A)(I) and (B)(I), respectively. The upper limit of component (C) is about 2 equivalents of component (C) for each equivalent of component (A)(I), and about two equivalents of component (C) for each equivalent of component (B)(I). Preferred amounts of the reactants are about 2 equivalents of the component (C) and from about 0.1 to about 2 equivalents of each of components (A)(II) and (B)(II) for each equivalent of

each of components (A) (I) and (B)(I). The ratio of equivalents of components (B) (I) to (A)(I) is greater than 2:1. As noted above, this ratio leads to the predominance of molecules in which B) (I) is linked to (B)(I). The ratio of (B) (I) to (A) (I) may range from 2:1 to about 10:1; or from 2.5:1 to 10:1. Preferred ranges are 2:1 to 5:1 or 2.5:1 to 5:1, and 2:1 to 4:1, or 2.5:1 to 4:1. A more preferred range is 2:1 to 3:1 or 2.5:1 to 3:1. The preferred ratio of high and low molecular weight species could be established early in the selection of the molecular weight of the starting materials (e.g. succinating a blend of high and low molecular weight olefins such as a blend of butylenes oligomers having from 16 to 36 carbon atoms) or the ratio could be established later such as after partial or complete synthesis and salting of the reaction product by mixing reaction products derived from other ratios of (B)(I) to (A)(I) (e.g. blending a salt of coupled (B)(I) (B)(I) product with a salt of a (B)(I) (A)(I) blend outside of the ratios specified).

The number of equivalents of the acylating agents (A)(I) and (B) (I) depends on the total number of carboxylic functions present in each. In determining the number of equivalents for each of the acylating agents (A) (I) and (B)(I), those carboxyl functions which are not capable of reacting as a carboxylic acid acylating agent are excluded. In general, however, there is one equivalent of acylating agent (A) (I) and (B) (I) for each carboxy group in these acylating agents. For example, there would be two equivalents in an anhydride derived from the reaction of one mole of olefin polymer and one mole of maleic anhydride. Conventional techniques are readily available for determining the number of carboxyl functions (e.g., acid number, saponification number) and, thus, the number of equivalents of each of the acylating agents (A) (I) and (B)(I) can be readily determined by one skilled in the art.

An equivalent weight of a polyamine is the molecular weight of the polyamine divided by the total number of nitrogens present in the molecule. If the polyamine is to be used as component (C), tertiary amino groups are not counted. On the other hand, if the polyamine is to be used as component



(A)(II) or (B)(II), tertiary amino groups are counted. Thus, ethylene diamine has an equivalent weight equal to one-half of its molecular weight; diethylene triamine has an equivalent weight equal to one-third its molecular weight. The equivalent weight of a commercially available mixture of polyalkylene polyamine can be determined by dividing the atomic weight of nitrogen (14) by the %N contained in the polyamine; thus, a polyamine mixture having a %N of 34 would have an equivalent weight of 41.2. An equivalent weight of ammonia or a monoamine is its molecular weight.

An equivalent weight of polyhydric alcohol is its molecular weight divided by the total number of hydroxyl groups present in the molecule. Thus, an equivalent weight of ethylene glycol is one-half its molecular weight.

An equivalent weight of a hydroxyamine which is to be used as component (C) is its molecular weight divided by the total number of  $-OH$ ,  $>NH$  and  $-NH_2$  groups present in the molecule. Thus, dimethylethanolamine when used as component (C) has an equivalent weight equal to its molecular weight; ethanolamine has an equivalent weight equal to one-half its molecular weight. On the other hand, if the hydroxyamine is to be used as components (A)(II) or (B)(II), an equivalent weight thereof would be its molecular weight divided by the total number of nitrogen groups present in the molecule. Thus, dimethylethanolamine, when used as component (A)(II) or (B)(II), would have an equivalent weight equal to its molecular weight; ethanolamine would also have an equivalent weight equal to its molecular weight.

An equivalent weight of an alkali metal is its atomic weight. An equivalent weight of an alkaline earth metal is the atomic weight divided by the valence.

The acylating agents (A)(I) and (B)(I) can be reacted with component (C) according to conventional ester- and/or amide-forming techniques. This normally involves heating acylating agents (A)(I) and (B)(I) with component (C), optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent. Temperatures of at least about  $30^{\circ}C$  up to the

decomposition temperature of the reaction component and/or product having the lowest such temperature can be used. This temperature is preferably in the range of about 50°C to about 130°C, more preferably about 80°C to about 100°C when the acylating agents (A)(I) and (B)(I) are anhydrides. On the other hand, when the acylating agents (A)(I) and (B)(I) are acids, this temperature is preferably in the range of about 100°C to about 300°C with temperatures in the range of about 125°C to about 250°C often being employed.

The reactions between components (A)(I) and (B)(I), and (A)(II) and (B)(II) are carried out under salt forming conditions using conventional techniques. Typically, components (A)(I) and (A)(II), and (B)(I) and (B)(II) are mixed together and heated to a temperature in the range of about 20°C up to the decomposition temperature of the reaction components and/or products having the lowest such temperature, preferably about 50°C to about 130°C, more preferably about 80°C to about 110°C; optionally, in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, until the desired product has formed.

The product of the reaction between components (A)(I) and (B)(I), and (A)(II) and (B)(II), respectively, must contain at least some salt linkage to permit said product to be effective as an emulsifier in accordance with the invention. Preferably at least about 10%, more preferably at least about 30%, more preferably at least about 50%, more preferably at least about 70%, and advantageously up to about 100% of components (A)(II) and (B)(II) that react with the acylating agents (A)(I) and (B)(I), respectively, form a salt linkage.

The following examples illustrate the preparation of the salt compositions of this invention. Unless otherwise indicated, in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, and all temperatures are in degrees centigrade.

#### EXAMPLE 1

1080 grams of polyisobutylene substituted succinic anhydride (number average molecular weight = 1048) and 818 grams of branched C<sub>16</sub>

hydrocarbyl-substituted succinic anhydride of molecular weight 322 were heated to a temperature between 92 and 98°C with stirring and maintained at that temperature for 45 minutes. 112 grams of ethylene glycol were added to the mixture. The mixture was maintained at a temperature  
5 between 92 and 98°C for 3 hours. 538 grams of triethanolamine are added to the mixture over a period of 0.5 hour. The mixture was maintained between 70-90°C for 1 hour then cooled to 50°C to provide the desired product. The ratio of equivalents of the low molecular weight substituted succinic anhydride to the high molecular weight substituted succinic  
10 anhydride was 2.5:1.

#### Functional Fluid Compositions

The functional compositions of the invention are oil-in-water emulsions which comprise a continuous water phase, a discontinuous organic phase, the emulsifying composition, and additives related to the  
15 function to be performed by the functional fluid. The discontinuous organic phase is preferably present at a level of at least about 1% by weight, more preferably in the range of from about 1% to about 50% by weight, more preferably in the range of from about 1% to about 20% by weight based on the total weight of emulsion. The continuous water phase is preferably  
20 present at a level of about 99% by weight, more preferably at a level in the range of from about 50% to about 99% by weight, more preferably from about 80% to about 99% by weight based on the total weight of said emulsion. The emulsifier blend of linear synthetic sulfonate and salt of the reaction product of a high molecular weight acylating agent, a lower  
25 molecular weight acylating agent and a coupling agent are preferably present at a level in the range of from about 1% to about 100% by weight, more preferably from about 20% to about 80% by weight based on the total weight of the organic phase. When the emulsifier is 100% of the organic phase, the emulsifier is acting to form an emulsion of itself in the water  
30 phase, and the organic phase is the emulsifier. Desirably the linear synthetic alkyl arenesulfonate is from about 10 to about 90 wt.% of the emulsifier blend and the salt of the reaction product is the complementary amount i.e.

10 to 90 weight percent. More desirably the linear synthetic alkyl arenesulfonate is from about 20 to 80 wt.%, and preferably from about 30 to 70 wt.% while the salt of the reaction product is from about 20 to 80 wt.% and more desirably from about 30 to about 70 wt.% of the emulsifier blend.

- 5 Optionally other surface active molecules may be present in the emulsifier blend for particular properties not easily achieved with the blend of two emulsifiers.

The oil can include most liquid hydrocarbons, for example, paraffinic, olefinic, naphthenic, aromatic, saturated or unsaturated hydrocarbons. In  
10 general, the oil is a water-immiscible, emulsifiable hydrocarbon that is either liquid at room temperature. Oils from a variety of sources, including natural and synthetic oils and mixtures thereof may be used.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as solvent-refined or acid-refined mineral oils of the paraffinic,  
15 naphthenic, or mixed paraffin-naphthenic types. Oils derived from coal or shale are also useful. Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, poly(alpha olefins), chlorinated polybutylenes; alkyl benzenes  
20 e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl) benzenes; hydroisomerized Fischer-Tropsch hydrocarbons; etc.; and the like.

Another suitable class of synthetic oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl  
25 succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, pentaerythritol, etc.). Specific  
30 examples of these esters include dibutyl adipate, di(2-ethylhexyl)-sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl

diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

5 Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

10 Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of useful oils. These include tetraethyl-silicate, tetraisopropylsilicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methylhexyl)-silicate, tetra(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxy)-di-siloxane, poly(methyl)-siloxanes, poly-(methylphenyl)-siloxanes, etc. Other useful synthetic oils include liquid esters of phosphorus-containing acid (e.g., tricresyl phosphate, trioctyl  
15 phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

Unrefined, refined and rerefined oils (and mixtures of each with each other) of the type disclosed hereinabove can be used. Unrefined oils are those obtained directly from a natural or synthetic source without further  
20 purification treatment. For example, a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except that they have been further treated in one or more purification  
25 steps to improve one or more properties. Many such purification techniques are known to those of skill in the art such as solvent extraction, distillation, hydrogenation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such  
30 rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed toward removal of spent additives and oil breakdown products.

Examples of useful oils include a white mineral oil available from Witco Chemical Company under the trade designation KAYDOL; a white mineral oil available from Shell under the trade designation ONDINA; and a mineral oil available from Pennzoil under the trade designation N-750-HT.

5        Optional additional materials may be incorporated in the composition of the present invention. Typical finished compositions may include lubricity agents, anti-wear agents, dispersants, corrosion inhibitors, other surfactants such as petroleum or synthetic alkyl sulfonates, metal deactivators, and the like. The emulsions of the present invention are shelf stable, which means  
10 they exhibit shelf stability of at least six months and typically one year or more.

A preferred method for making the emulsions of the invention comprises the steps of (1) mixing the emulsifier with the oil phase, (2) mixing the additives with the oil phase, (3) stirring the oil phase with the water  
15 phase to form a oil-in-water emulsion. Mixing of the oil with the appropriate additives may be conducted in any suitable mixing apparatus. Any type of apparatus capable of either low or high shear mixing may be used to mix the oil and water phases to prepare these oil-in-water emulsions.

#### Examples of Functional Fluids

20        Example A illustrates a functional fluid oil-in-water emulsion within the scope of the invention. The example is illustrative but does not limit the scope of the invention.

#### Example A

A emulsifier blend was prepared by mixing the product of Example 1  
25 (60.0 wt.%) with a commercial available synthetic alkyl arenesulfonate from C14-C16 alkyls grafted to benzene and sulfonated (40 wt.%). Both surfactants were used as received and were not 100% active. An emulsifier package was prepared from 20 wt.% of the emulsifier blend and 80 wt.% of a naphthenic mineral oil. Five mL of the concentrated emulsifier package  
30 were mixed with 95 mL of water to form the emulsion metal working fluid.

The emulsifier blend of Example A performed comparable to a natural petroleum sulfonate standard used in metalworking formulations in both soft

and hard water. Slightly better performance was noted in Example A when the counter ion was triethanol amine rather than other alkanol amines (better performance was generally indicated by more of the oil phase being spontaneous emulsified with minimal agitation as the proportion of emulsifier in the emulsifier package was decreased).

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. It is to be understood that the invention disclosed herein is intended to cover such modifications.